CHARACTERIZATION AND PROPERTIES OF SODIUM HYDROXIDE/UREA REGENERATED CELLULOSE REINFORCED POLY(3-HYDROXYBUTYRATE) BIOCOMPOSITES

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ABSTRACT

Pure cellulose was dissolved in 7 wt.% natrium hydroxide (NaOH)/12 wt.% urea at the temperature of -12 °C to prepare the regenerated cellulose (RC). Structural, morphological and thermal properties of cellulose and RC were compared using field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results revealed decreased in crystallinity, reduced of FTIR peak intensity and decreased the thermal stability of RC sample. FESEM results showed that the morphological of RC became more spherical. RC/poly(3-hydroxybutyrate) (PHB) biocomposites were prepared by melt mixing in internal mixer with different RC content (1, 3, 5 and 7 wt.%). The structural, morphological, thermal and mechanical properties of the RC/PHB were characterized. From the XRD, the crystallinity was decreased with the increasing of RC fiber loading. The melting temperature of biocomposites was found to increase upon the increasing of RC fiber. TGA results indicated that the char residue and onset temperature of biocomposites were decreased with the increasing of RC loading. Increased loading of RC decreased the tensile strength and elongation at break, while the Young's modulus showed the optimum value at 5 wt.%. Based on flexural strength and flexural modulus, 3 wt.% RC was the optimum amount for PHB composite. As for comparison of PHB composite with 3 wt.% cellulose and 3 wt.% RC, DSC result showed the melting point of 3 wt.% RC/PHB composite was higher than 3 wt% cellulose/PHB composite. The tensile properties and impact strength were higher for cellulose/PHB compared to RC/PHB composites, while flexural properties of RC/PHB were higher than cellulose/PHB composites.

ABSTRAK

Selulosa tulen dilarutkan di dalam larutan akueus 7 wt.% natriun hidroksida (NaOH) / 12 wt.% urea pada suhu -12 °C untuk menyediakan selulosa terjanasemula (RC). Struktur, morfologi dan sifat haba selulosa dan RC dibandingkan menggunakan mikroskop elektron imbasan pancaran medan (FESEM), spektroskopi inframerah transformasi Fourier (FTIR), pembelauan sinar-x (XRD), analisis termogravimetri (TGA) dan kalorimetri imbasan pembezaan (DSC). Keputusan sample RC menunjukkan penurunan kehabluran, penurunan intensiti puncak FTIR dan penurunan kestabilan haba. Keputusan FESEM menunjukkan bahawa morfologi RC menjadi lebih berbentuk sfera. RC/poli(3-hidroksibutirat) (PHB) biokomposit telah disediakan dengan pencampuran leburan dengan kandungan RC yang berbeza (1, 3, 5 dan 7 wt.%) dalam pengadun. Struktur, morfologi, sifat haba, sifat mekanik RC/PHB telah dicirikan. Daripada keputusan XRD, kehabluran telah menurun dengan peningkatan gentian RC. Suhu lebur biokomposit didapati meningkat dengan penambahan gentian RC. Keputusan TGA menunjukkan sisa hangus dan suhu permulaan RC/PHB telah menurun dengan peningkatan kandungan RC. Peningkatan RC telah menurunkan sifat kekuatan tegangan dan pemanjangan pada takat putus, manakala modulus Young menunjukkan nilai optimum pada 5 wt.% gentian RC. Berdasarkan kekuatan lenturan dan modulus lenturan, 3 wt.% RC adalah nilai optimum bagi komposit PHB. Dalam perbandingan antara 3 wt.% selulosa dan 3 wt.% RC, kajian DSC menunjukkan takat lebur komposit 3 wt.% RC/PHB adalah lebih tinggi, berbanding komposit 3 wt.% selulosa/PHB. Sifat tegangan dan kekuatan impak komposit selulosa/PHB adalah lebih tinggi daripada komposit RC/PHB, manakala sifat lenturan komposit RC/PHB adalah lebih tinggi daripada komposit selulosa/PHB.

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LIST OF ABBREVIATIONS

AR	-	Analytical Reagents
ASTM	-	American Society for Testing and Materials
BCNW	-	Bacterial Cellulose Nanowhiskers
CSF	-	Cellulose Standard Fiber
CNF	-	Cellulose Nano Fiber
NaOH	-	Sodium Hydroxide
CS_2	-	Carbon Disulfide
DTG	-	Derivative Thermogravimetry
DSC	-	Differential Scanning Calorimetry
FTIR	-	Fourier Transform Infrared Spectroscopy
H_2SO_4	-	Sulfuric Acid
H_2O	-	Water
IC	-	Inclusion Complex
LCCE	-	Long Chain Cellulose Ester
MCCF	-	Microcrystallite Cellulose Fiber
NA_2SO_4	-	Sodium Sulfate
OH group	-	Hydroxyl Group
phr	-	Part per hundred resin
PHA	-	Polyhydroxyalkanoates

PHB	-	Poly(3-hydroxybutyrate)
PHBV	-	Poly(3-hydroxybutyrate-co-3- hydroxyvalerate)
PP	-	Polypropylene
rpm	-	Rotation per minute
PCL	-	Poly(ε-caprolactone)
PLA	-	Polylactic Acid
SEM	-	Scanning Electron Microscope
TGA	-	Thermogravimetric Analyse
wt. %	-	Weight percentage
XRD	-	X-ray Diffractometer

LIST OF SYMBOLS

F	-	Force
g	-	Gravity = 9.81 m/s
p	-	Pressure
p	-	Density
T	-	Temperature

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Polymer composites are mixtures of polymer matrix with additives, which will form two or more phases and components ((Xanthos *et al*., 2010). There are two types of additives, which are organic and inorganic, where involving much geometry such as spheres, fibers, particulates and flakes.

The development of commercial petroleum based synthetic polymer beneficial for decades. However, it causes severe problems like environmental pollution and over exploitation of fossil resources. The most possible way to develop raw materials that environmentally compatible is by preparing the biodegradable bioploymers (Hatakeyana *et al*., 2002). Nowadays, there are many research using renewable resource natural fiber in the polymer composites as a reinforcements. These bring benefits to the environment with respect to the biodegradable and utilization of natural materials (Rout *et al.*, 2001).

Poly(3-hydroxybutyrate) (PHB) is one of the biopolymers, which produced by saturated aliphatic polyester. It can be synthesized by variety type of bacteria as a metabolism of stored energy molecule (Mokhtari-Hosseini *et al.,* 2009). PHB is a semicrystalline polymers that biodegradable and has biocompatibility. PHB is mainly used in biomedical field and helping to relieve environmental pollution due to the disposal of non biodegradable petroleum based polymer (Savenkova *et al.,* 2000).

Cellulose is a semicrystalline polysaccharide which has large amount of hydroxyl groups that responsible for the hydrophilic properties of the natural fibers (Schuster *et al.,* 2004). It is the basic building block in most of the plants (Krassig *et al.,* 1993). Cellulose is a carbohydrate polymer generated from the repeating β-D-glucopyranose molecular units that are covalently linked between the equatorial OH group of C1 carbon atom and C4 carbon atom. Cellulose is an extensive and linear-chain polymer, consists a large number of hydroxy functional groups. Chain length of cellulose determined by the degree of polymerization, depend on the treatment and origin of the raw material. Structure of cellulose chain consists a D-glucose unit (C4-OH) at one end, while the other end is C1-OH group (Klemm *et al.,* 2005a).

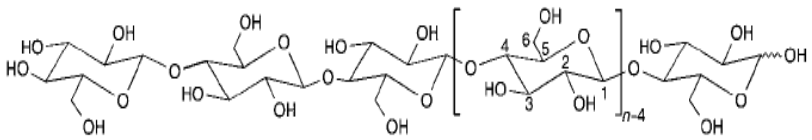

Figure 1.1: Molecular structure of cellulose (n= degree of polymerisation)(Klemm *et al.*, 2005a)

Due to renewable and environmentally friendly biomaterial, plant cellulose contributes about 2×10^{12} tons of the annually biomass production, which are photosynthesized by the fixation of carbon dioxide in sea and land (Klemm *et al.,* 2005a). The advantages of the used of cellulose applications are the hydrophilicity, biocompatibility and the production of cellulose composite with either biopolymer or synthetic polymers (Kim *et al.,* 2006). It also exhibited wide applications. Cellulose is biodegradability, abundance, stiffness and high mechanical strength. Besides this, cellulose also exhibit low weight and price, and the characteristics such as a very large surface-to-volume ratio and outstanding electrical, mechanical and thermal properties thus became the most abundant renewable biopolymer material (Gabr *et al.,* 2014).

Cellulose powder used as raw material in different type of applications including packaging, drugs, paints and toothpaste. In its original form, cellulose is

classified as the cellulose I, which also called native cellulose. After undergo mechanical or chemical treatment, the cellulose is classified as cellulose II, which also called as regenerated cellulose (RC) (Kompella and Lambros, 2002). Crystalline structure of native cellulose exist as cellulose I, formed by two polymorphs: triclinic (Ia) and monoclinic (Ib) which appear alongside each other. Varies origin of cellulose have different Ia/Ib.

Cellulose application and development are limited due to its difficulty to dissolve in most of the common solvents due to its strong inter-molecular force, van der Waals and intra-molecular force of hydrogen bonds (Heinze and Koschella, 2005). Other than that, the cellulose also does not melt, making it difficult to be processed using common processing method. Moreover, traditional technologies that produce RC materials are not environmental friendly causing serious environmental problem and pollution. Therefore, processing approaches that prevent toxic byproducts and complicated processing routes is important (Guansen *et al.*, 2012).

Sodium hydroxide (NaOH)/urea aqueous solvent system have been reported as a good alternatif and green solvent of cellulose. NaOH and urea are inexpensive and nontoxic chemical agents. NaOH treatment or dissolution of the cellulose followed by precipitation can be used to form cellulose II. Cellulose II have an antiparallel orientation, in contrast to native cellulose I which have parallel chains. This conversion cannot be reversed, indicating that cellulose II is stable (Osullivan *et al.*, 1997).There is no evaporation of any toxic byproducts at the time of cellulose dissolution at low temperature. During the commercialize and large scale production, this aqueous system can maintain “green” atmosphere air in the surrounding environment. The byproducts also can be easily recycled or separated. (Qi *et al.*, 2009).

1.2 Problem Statement

Recently, there is a great interest in the study of PHB biopolymers, driven by it biodegradability however it has limited range of applications due to its high production cost and low mechanical properties. Due to high crystallinity, PHB is brittle and stiff thus reduced the mechanical properties of PHB with a low extension at break, which limit the use of PHB (Seggiani *et al.*, 2015).

Cellulose is abundant and relatively cheap resources. Cellulose fibers have the advantages of renewable, nontoxic, biodegradable and easily obtained from natural raw materials. Their commercial usage has been limited because they have lower thermal, mechanical and gas barrier properties if compared to synthetic polymers. However, cellulose can be incorporated into polymer matrix to enhance thermal and mechanical properties. Cheng *et al.* (2007) studied the lyocell regenerated cellulose fiber and microfibrillated cellulose to reinforce polyvinyl alcohol. The tensile modulus found to improve as increasing amount of lyocell and microfibrillated cellulose fiber, especially at filler content of in between 2% to 6%.

In the research of Viviana *et al.* (2009), the double layer of PHB composite with acetylated cellulose cardboard found to have a better interfacial adhesion compared to the PHB/pure cellulose cardboard composites. This is due to diminish of hydrophilic properties of cellulose, and increased in interfacial adhesion with PHB. Mechanical properties of polymer composites can be affected depending on the cellulose treatment. In the research of Dormann *et al.* (2016) on all-cellulose composite laminates, with short dissolution time in the aqueous of 7 wt.% NaOH/12 wt.% urea of 5 min led to improvement in tensile strength of 114 MPa and a Young's modulus of 7.8 GPa. Thus, NaOH/urea treatment has potential to develop an environmental friendly fiber biocomposite. Through the regeneration process, the morphology of RC fiber would change thus improving mechanical and thermal properties due to higher interfacial adhesion of RC fiber to PHB matrix as compared to cellulose fiber.

This study focused on preparation of RC and the effects of RC loading on PHB properties. RC was prepared using NaOH/urea aqueous solution due to simple preparation, economical, environmental friendly and fast dissolubility. Effect of the RC fiber loading ratio in PHB matrix was investigated, in order to find the optimum loading ratio of RC fibers on thermal, mechanical, structural and morphology properties of composites.

1.3 Objective

The overall objective is to develop a biocomposites based on PHB/RC.

The specific objectives are:

1. To prepare the RC via NaOH/urea aqueous and characterize the morphological and thermal properties.

2. To investigate the effects of RC content on the morphology, mechanical and thermal properties of PHB/RC biocomposites.

3. To compare the properties of PHB composites of 3 wt% of cellulose and RC.

1.4 Scopes of the Study

The scope of study includes the following criteria:

(i.) From the purchased cellulose powder, the RC fiber were prepared using urea/ NaOH regeneration process.

(ii.) The RC fiber were mixed with PHB in internal mixer. Then, the compound were hotpress in compression machine into suitable thickness for mechanical testing.

(iii.) The sample were cut into suitable dimension, then were characterized using:

a. Thermogravimetric Analyser (TGA)

TGA was used to measure thermal stability of the material. The tests were performed non-isothermally at constant heating rate to obtain the onset of thermal degradation and char residue.

b. Differential Scanning Calorimetry (DSC)

DSC testing was used to measure the melting temperature, glass transition temperature, crystallization temperature and crystallinity.

c. Tensile testing

Tensile testing was one of the mechanical testing. The samples were subjected to a tensile force in constant force. Values of tensile strength, tensile modulus and elongation at break were obtained.

d. Flexural testing.

Flexural testing method was used to measure behavior of materials when subjected to three points loading. Flexural strength, and flexural modulus were provided.

e. Izod Impact Tester.

The Izod impact tester was used to determine the impact resistance and amount of energy that absorbed by material in order to fracture. Notch was cut across the testing sample. Pendulum hammer was release and hit the sample to break it. Impact energy was recorded.

f. Field Emission Scanning Electron Microscopy (FESEM)
FESEM gives the high magnification and resolution images by focus the electron beam across material surface. It is used to examine the interface, size and surface of the materials.

g. X-ray Diffractometer (XRD)
The percentage crystallinity in the material was identified.

h. Fourier Transform Infrared Spectroscopy (FTIR)
FTIR was used to identify the chemical functional group in material.

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